



## Editor Choice Paper

# Synthesis and characterization of new rhodium and iridium complexes with trianisylphosphine, $\text{PAn}_3$ , and evaluation of their catalytic behavior in the homogeneous hydrogenation of cinnamaldehyde

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## ABSTRACT

A new family of rhodium and iridium compounds with the bulky tris(*ortho*-methoxyphenyl) phosphine ( $\text{PAn}_3$ ) was synthesized and characterized by NMR methods. The X-ray crystal structures of  $\text{RhCl}(\text{PAn}_3)(\text{COD})$  (**1**) and  $\text{Ir}[(\text{PBz}_3)(\text{PAn}_3)(\text{COD})]\text{PF}_6$  (**4**) have been determined. A stabilizing agostic interaction has been crystallographically observed in both compounds, due to the steric hindrance of the *ortho*-substituted phosphine ligand and its presence has been associated to the fluxional behavior shown by the complexes on the NMR timescale in solution. Iridium complexes containing  $\text{PBz}_3$  and/or  $\text{PAn}_3$  have been evaluated as catalyst precursors for the hydrogenation of *trans*-cinnamaldehyde (CNA), and their activities have also been compared to those of other iridium complexes containing bulky phosphine ligands, such as  $\text{PTol}_3$  (tris-*ortho*-tolyl-phosphine). The catalytic experiments show that irrespectively of the phosphine combination, all of the evaluated catalysts prevalently hydrogenate the C=C moiety. However, the product selectivity can be tuned by changing either the substrate/catalyst ratio or the phosphine ligand at the metal center. The catalyst with  $\text{PAn}_3$  proved to be more efficient and also gave higher yields of the enol product, indicating that stereoelectronic effects are responsible for the changes in selectivity.

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## 1. Introduction

The decoration of phenyl rings with different substituents in aromatic phosphine ligands has become one of the most effective ways to tune the electronic and steric properties of these ligands and to get the most out of catalytic systems [1,2]. Methoxy ( $\text{OCH}_3$ ) substituents have played a major role in these modifications [2–9], specially when these are performed in *ortho* position, since they can electronically tune the properties of the ligand as well as create important steric effects.

Several reports [3–8] have appeared regarding the coordination chemistry of methoxyphenyl phosphines with more than one substituent in the aromatic ring. As an example, it is worth mentioning the in-depth studied family of ligands derived from 2,6-dimethoxyphenyl groups, MDMPP, BDMPP and TDMPP [3–6] (Fig. 1), which show multiple hapticity since the coordination may

occur not only through the phosphorus atom, but also through at least one of the oxygen atoms from the methoxy groups [4,6]. Also, low coordination numbers can be stabilized using this kind of ligands as well as the more encumbering trisubstituted TMPP [6].

Chiral methoxyphenyl phosphine ligands have been reported [7,8] and among these, DIPAMP (Fig. 1) is the most successful case [7]. Also, interesting synthetic methodologies have been developed to obtain methoxy-substituted phosphine ligands with polar groups [9]. However, regardless of the interesting properties observed with these ligands, the simpler tris(*ortho*-methoxyphenyl)phosphine, hereafter tris(*ortho*-anisyl)phosphine ( $\text{PAn}_3$ ), has received only little attention [10–14]. Among miscellaneous results, comparative studies on the basicity of  $\text{PAn}_3$  and other phosphines have been carried out by evaluating the formation of ionic pairs of gallium (III) with  $\text{PR}_3$  [10]. The reactivity of a number of tertiary phosphine ligands, including  $\text{PAn}_3$ , towards  $(\text{Ph}_2\text{Se}_2\text{I}_2)_2$  has been reported [11] while some (*ortho*-anisyl)phosphides were also described [12].

The coordination chemistry of  $\text{PAn}_3$  has attracted scarce attention, essentially confined to  $\text{M}(\text{CO})_6$  derivatives ( $\text{M} = \text{Cr}, \text{Mo}, \text{W}$ )

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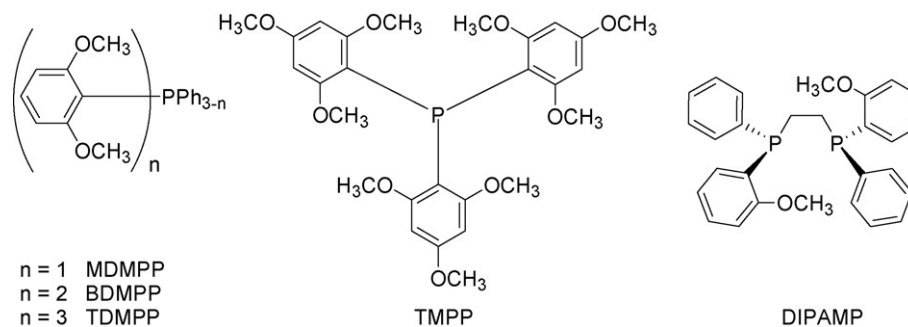


Fig. 1. Examples of methoxyphenylphosphines from the literature [4,6,7].

[13] and gold complexes [14]. To the best of our knowledge, only one rhodium(I) compound with  $\text{PAN}_3$ , namely  $\text{RhCl}(\text{PAN}_3)(\text{COD})$ , COD = 1,5-cyclo-octadiene, has been briefly described [15] without any crystallographic data. Also, one Rh(II) species containing  $\text{PAN}_3$  has been reported [16]. In contrast, no iridium/ $\text{PAN}_3$  complex has been mentioned and no catalytic study involving  $\text{PAN}_3$  complexes has been reported.

Herein, we report the synthesis and characterization of a family of rhodium and iridium complexes with tris(*ortho*-anisyl)phosphine ( $\text{PAN}_3$ ) and describe the solid state structure of two exemplificative species like  $\text{RhCl}(\text{PAN}_3)(\text{COD})$  and  $[\text{Ir}(\text{PBz}_3)(\text{PAN}_3)(\text{COD})]\text{PF}_6$ . The catalytic properties of some of these species in the hydrogenation of *trans*-cinnamaldehyde (CNA) have also been studied, since the production of allylic alcohols like cinnamyl alcohol or cinnamol has importance due to their potential use as building blocks in organic synthesis [17]. Finally, a comparison of the catalytic properties of Ir/ $\text{PAN}_3$  precursors with respect to other complexes bearing other bulky phosphine ligands, such as  $\text{PBz}_3$  [18] or  $\text{PTol}_3$  is reported.

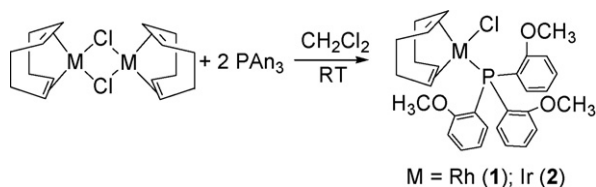
## 2. Results and discussion

### 2.1. Synthesis and characterization of $\text{MCl}(\text{PAN}_3)(\text{COD})$ ( $\text{M} = \text{Rh}, \text{Ir}$ )

The binuclear complexes  $[\text{MCl}(\text{COD})]_2$  ( $\text{M} = \text{Rh}, \text{Ir}$ ) react with two equivalents of  $\text{PAN}_3$  under mild conditions ( $\text{CH}_2\text{Cl}_2$ , room temperature), to give bright yellow crystals of the neutral complexes  $\text{MCl}(\text{PAN}_3)(\text{COD})$  [ $\text{M} = \text{Rh}$  (**1**), Ir (**2**)] in high yield (>90%) (Scheme 1). Compounds **1** and **2** are air-stable in the solid state and are soluble in polar organic solvents.

An alternative lower yield synthesis of compound **1** has already been reported by Tiburcio et al. [15]. Crystals of **1** suitable for an X-ray diffraction analysis were grown from a dichloromethane/ethanol solution. An ORTEP drawing showing the structure of compound **1** is given in Fig. 2. A summary of crystal data and a selection of bond distances (Å) and angles (°) are collected in Tables 1 and 2.

Complex **1** crystallizes in a monoclinic system with a  $P2_1/n$  space group. The molecular structure is a strongly distorted square planar one, reflecting the presence of the bulky phosphine ligand. The



Scheme 1.

Table 1

Summary of Crystal Data for  $\text{RhCl}(\text{PAN}_3)(\text{COD})$  (**1**) and  $[\text{Ir}(\text{PBz}_3)(\text{PAN}_3)(\text{COD})]\text{PF}_6$  (**4**).

	<b>1</b>	<b>4</b>
Formula	$\text{RhC}_{29}\text{H}_{33}\text{ClO}_3$	$\text{C}_{50}\text{H}_{54}\text{F}_6\text{IrO}_3\text{P}_3$
Mol. wt.	598.88	1102.04
Cryst size (mm)	$0.65 \times 0.35 \times 0.45$	$0.52 \times 0.20 \times 0.13$
Cryst. syst.	Monoclinic	Triclinic
Space group	$P2_1/n$	$P_{-1}$
<i>a</i> (Å)	8.559 (3)	10.1516 (19)
<i>b</i> (Å)	18.046 (2)	20.521 (4)
<i>c</i> (Å)	17.004 (3)	24.595 (3)
$\beta$ (degree)	90.144 (19)	100.728 (14)
<i>V</i> (Å <sup>3</sup> )	2626.4(11)	5034.1 (16)
<i>Z</i>	4	4
<i>d</i> <sub>calc</sub> (mg/m <sup>3</sup> )	1.515	1.454
Abs. coeff. (mm <sup>-1</sup> )	0.842	2.808
<i>F</i> (000)	1232	2216
$\theta$ range (degree)	2.26–24.97	2.04–22.98
Index ranges	$-10 \leq h \leq 10$ $0 \leq k \leq 21$ $0 \leq l \leq 20$	$-11 \leq h \leq 10$ $0 \leq k \leq 22$ $0 \leq l \leq 27$
Tot. number of data	4778	7152
Number of unique data, $I \geq 2\sigma(I)$	4617 [ <i>R</i> (int)=0.0196]	6966
<i>S</i> (goodness of fit on <i>F</i> <sup>2</sup> )	1.024	0.851
<i>R</i> 1 ( $I \geq 2\sigma(I)$ )	0.0310	0.0481
<i>wR</i> 2 (all)	0.0700	0.1317
Largest diff. peak and hole (e/Å <sup>3</sup> )	0.339, –0.334	1.290, –0.773

Table 2

Selected bond distances (Å) and angles (°) for  $\text{RhCl}(\text{PAN}_3)(\text{COD})$  (**1**) and  $[\text{Ir}(\text{PBz}_3)(\text{PAN}_3)(\text{COD})]\text{PF}_6$  (**4**).

	<b>1</b>	<b>4</b>	
Bond distances			
Rh(1)–C(1)	2.108(3)	Ir(1)–C(4)	2.189(10)
Rh(1)–C(2)	2.131(3)	Ir(1)–C(2)	2.211(10)
Rh(1)–C(3)	2.156(4)	Ir(1)–C(3)	2.193(11)
Rh(1)–C(4)	2.184(4)	Ir(1)–C(1)	2.212(11)
Rh(1)–P(1)	2.3548(9)	Ir(1)–P(2)	2.349(3)
Rh(1)–Cl(1)	2.3803(11)	Ir(1)–P(1)	2.361(2)
Bond angles			
P(1)–Rh(1)–Cl(1)	89.25(4)	C(4)–Ir(1)–C(2)	89.0(4)
C(1)–Rh(1)–C(2)	38.11(15)	C(4)–Ir(1)–C(3)	35.5(4)
C(1)–Rh(1)–C(3)	95.14(16)	C(2)–Ir(1)–C(3)	79.2(4)
C(2)–Rh(1)–C(3)	80.75(15)	C(4)–Ir(1)–C(1)	78.7(5)
C(1)–Rh(1)–C(4)	80.18(16)	C(2)–Ir(1)–C(1)	35.8(5)
C(2)–Rh(1)–C(4)	89.17(15)	C(3)–Ir(1)–C(1)	90.5(5)
C(3)–Rh(1)–C(4)	36.54(17)	C(4)–Ir(1)–P(2)	91.5(3)
C(1)–Rh(1)–P(1)	95.87(10)	C(2)–Ir(1)–P(2)	159.8(4)
C(2)–Rh(1)–P(1)	93.82(10)	C(3)–Ir(1)–P(2)	89.5(3)
C(3)–Rh(1)–P(1)	154.18(15)	C(1)–Ir(1)–P(2)	162.8(4)
C(4)–Rh(1)–P(1)	169.28(14)	C(4)–Ir(1)–P(1)	163.9(4)
C(1)–Rh(1)–Cl(1)	155.69(12)	C(2)–Ir(1)–P(1)	90.3(3)
C(2)–Rh(1)–Cl(1)	165.30(11)	C(3)–Ir(1)–P(1)	159.0(4)
C(3)–Rh(1)–Cl(1)	90.25(12)	C(1)–Ir(1)–P(1)	91.4(3)
C(4)–Rh(1)–Cl(1)	90.45(12)	P(2)–Ir(1)–P(1)	94.67(9)

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